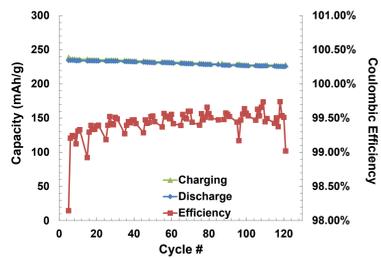


## Introduction

High capacity manganese rich positive electrode materials (HCMR™) are promising candidates for high-energy lithium ion batteries used in plug-in hybrid (PHEV) electrical vehicles. HCMR™ material has capacity of >230 mAh/g at operation potentials between 2.0 - 4.6 V.

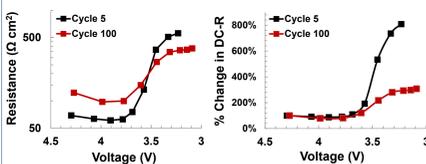
### Half cell performance



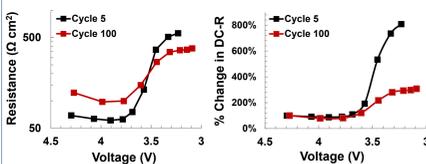
### Technical limitations and challenges

- Discharge voltage profile fade with cycling
- Operation outside of electrolyte stability window
- Large rise in resistance within every cycle correlating with cell voltage

### Resistance from discharge pulse



### DC-R change in percent



- Significant DC-R changes within a single discharge as well as prolonged cycles
- Dynamics of DC-R changes during discharge diminishes with cycling

### Possible DC-R rise scenarios

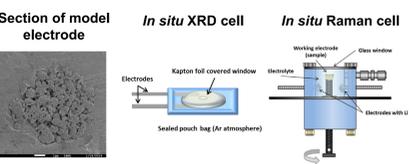
- Evidence of Structural Transformation with Cycling and Proposed Strategies Using Lithium and Transition Metal Substitutions
- Ionic and Electronic Barriers at Interphases and Interfaces
- Loss of Mechanical Integrity in HCMR™ Material - Changes in Morphology and Topology

## Experimental

Pristine HCMR™ powder and composite electrodes were supplied by Envia Systems.

Variety of common analytical techniques were applied such as (S)TEM, EELS, Raman spectroscopy, PITT, FT-IR spectroscopy, EIS, SEM and circuit modeling. Model binder-less and carbon free HCMR™ electrodes were prepared by pressing powder particles into the aluminum current collector.

The electrodes were tested in 2023 coin cells and *in situ* spectro-electrochemical cells.



## Acknowledgements

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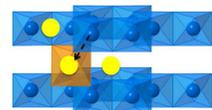
Work at the National Center of Electron Microscopy, Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under the Contract No. DE-AC02-05CH11231.

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## 1. Evidence of Structural Transformation with Cycling and Proposed Strategies Using Lithium and Transition Metal Substitutions

### First-principles study of the structural stability of (Li<sub>2-x</sub>A<sub>x</sub>)(Mn<sub>1-y</sub>B<sub>y</sub>)O<sub>3</sub>



Prototype formula:  
(Li<sub>2-x</sub>A<sub>x</sub>)(Mn<sub>1-y</sub>B<sub>y</sub>)O<sub>3</sub>  
A: Na, K, Mg  
B: T, V, Co, Ni, W, Ru

- $\Delta E = E(\text{after B migration}) - E(\text{before B migration})$
- Mn replacement is more influential than Li replacement on determining if  $\Delta E$  is positive (B migration is unfavorable) or negative (B migration is favorable)

### The effect of doping

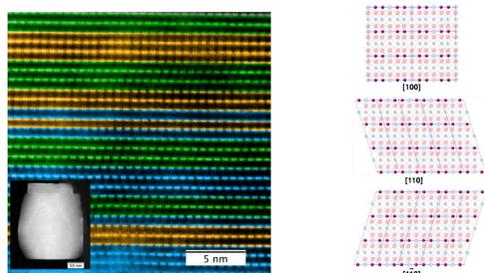
Changes in potential and kinetic energy of electron-nucleus interactions upon Mn migration in A<sub>0.042</sub>B<sub>x</sub>Mn<sub>1-x</sub>O<sub>3</sub>, (A: Na or K, B: Co or Ni)

Li-replacement (A)	Mn-replacement (B)	$\Delta E$ (eV) in x=0.5	$\Delta E$ (eV) in x=0.375	$\Delta E$ (eV) in x=0.25
K	Co	2.22	-2.16	-2.67
K	Ni	2.02	1.59	-8.55
Na	Co	0.47	-1.33	-0.68
Na	Ni	1.64	2.44	-7.60

- At high Mn content (lower material cost), K and Ni doping is better choice than K and Co
- Due to large size mismatch between Na<sup>+</sup> (1.16 Å), K<sup>+</sup> (1.52 Å) and Li<sup>+</sup> (0.9 Å), the Li-replacements have to distribute evenly among the material to reduce strain energy

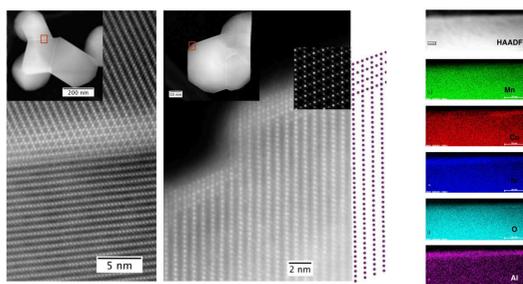
### Structural studies on HCMR™ material

#### Pristine: bulk structure



- Li- and Mn-rich transition metal oxides consist of randomly-sized monoclinic domains. The HAADF STEM image shows [100], [110] and [1-10] domains of the monoclinic phase stacked on (001) planes.
  - This arrangement is observed throughout the primary particle, confirming that the bulk is made of a single phase (except for defects and surface layer).
  - Similar structure was observed for materials with similar composition made at LBNL and another commercial material (TODA HE5050).
- XEDS maps do not show any segregation of Mn

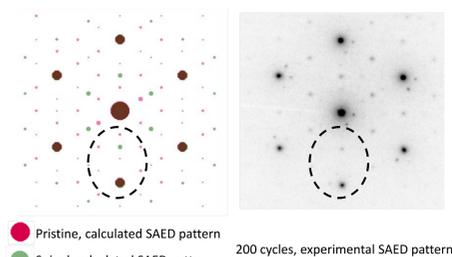
#### Pristine material: surface structure



- XEDS shows Ni and Co enrichment and O depletion at the surface
- 2-3 nm thick spinel phase observed on certain facets of primary particles
- The orientation relationship between the bulk monoclinic phase and surface spinel is as follows:

$$(001)_M \parallel (1\bar{1}1)_S, [010]_M \parallel [001]_S$$

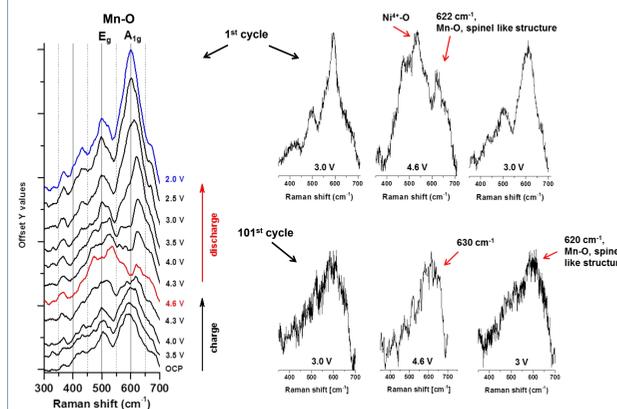
#### Cycled material: bulk structure changes



- Preliminary (S)TEM studies of HCMR™ material after 1 cycle shows negligible change of the spinel surface layer thickness.
- Electron diffraction and HRTEM studies after 200 cycles clearly show phase transformation of the bulk material. The structure of this new phase is under investigation. Preliminary results show a possibility of spinel structure.

## 2. Ionic and Electronic Barriers at the Interphase and Interface

### Studies of interphases in HCMR™ material by *in situ* Raman spectroscopy



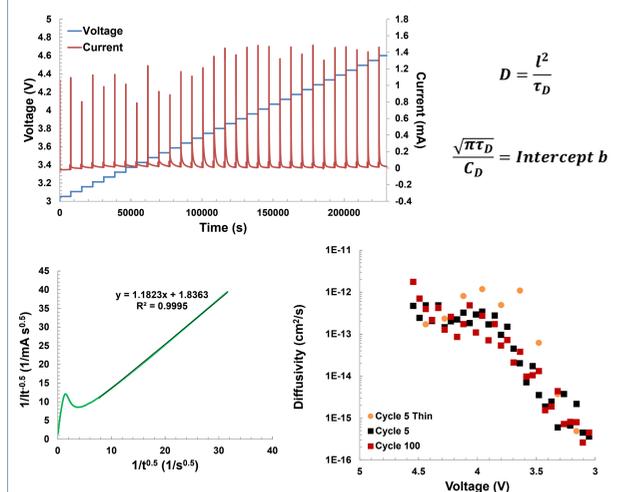
### Surface changes to a spinel like structure from the following observations:

- In the 1<sup>st</sup> cycle A<sub>1g</sub> band of Mn-O at 595 cm<sup>-1</sup> disappears during delithiation, new band emerges at 622 cm<sup>-1</sup>
- After 1<sup>st</sup> cycle, A<sub>1g</sub> band shifts slightly to higher wavenumbers
- The 622 cm<sup>-1</sup> peak intensity increases with cycling
- Significant band broadening may indicate higher content of Mn<sup>3+</sup>

### Changes in surface transition metal activity:

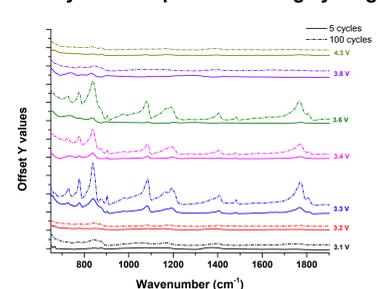
- Ni<sup>4+</sup>/Ni<sup>2+</sup> redox reactions observed during 1<sup>st</sup> cycle
- No Ni<sup>4+</sup>/Ni<sup>2+</sup> redox reactions observed after 100 cycles

### Li<sup>+</sup> diffusivity in HCMR™ quantified by Potentiostatic Intermittent Titration Technique (PITT)



- Li<sup>+</sup> diffusivity changes dramatic below 3.8 V within a cycle
- No change of Li<sup>+</sup> diffusivity in HCMR™ material with prolonged cycling

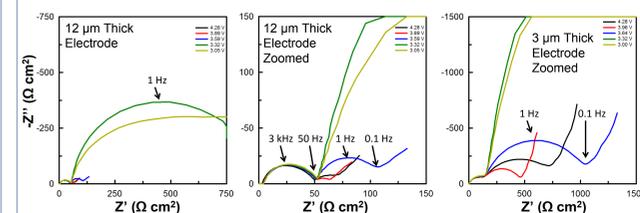
### Electrolyte decomposition during cycling



- The composition and thickness of the surface layer of the electrolyte decomposition products strongly varies during each cycle, and gradually increases with cycling
  - Spectral signature of the surface layer most visible at 3.3 - 3.6 V
  - FTIR signal greatly reduced at fully lithiated and delithiated state
- Surface layer creates electronic and ionic barriers between the primary particles of HCMR™ and within the composite electrode

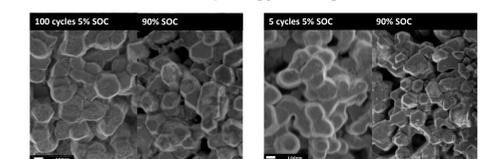
## 3. Loss of Mechanical Integrity - Changes in Morphology and Topology

### HCMR™ electrode impedance variations during cycle 5



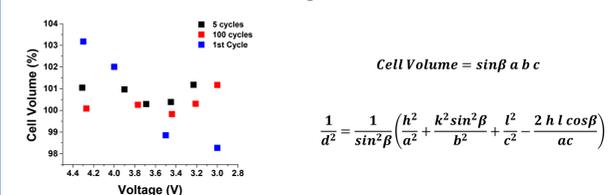
- Electrode impedance correlates with cell voltage
- Impedance increases within each cycle at time scales typical of solid state diffusion
- Thinner composite electrodes more clearly show impedance associated with diffusion

### HCMR™ material secondary particles morphology and topology changes

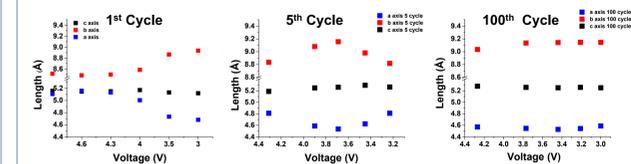


- Large gaps and crevices are observed between the primary particles inside of the secondary particles
- Particle surface morphology changes within a cycle possible surface film formation
- No dramatic changes of particle surface morphology after prolonged cycling

### Monoclinic unit cell changes of the HCMR™ material

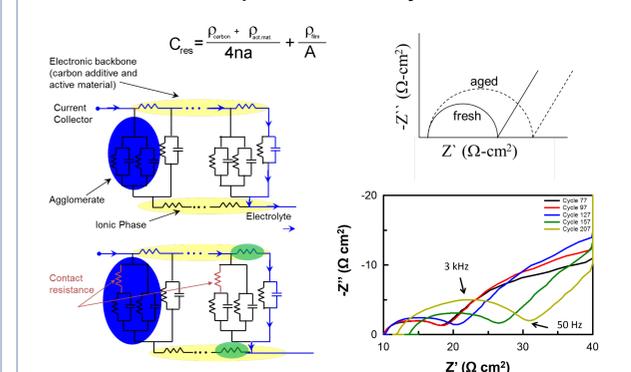


- Cell volume calculated assuming monoclinic structure
- Change in cell volume decreases with cycling



- Monoclinic cell a and b axis change during each cycle
- Monoclinic c axis remain nearly constant with cycling

### Effect of contact resistance increase in a distributed composite electrode system



- Diameter of high frequency semicircle increase in size with cycling (red resistor)
- Impedance high frequency intercept shifts with cycling (green resistor)

## Summary

- Preliminary evaluations of HCMR™ materials suggest that the primary particles are single phase, aperiodic crystals consisting of monoclinic domains
  - Specific surface planes of the primary particle form a 2-3 nm spinel structure
  - Spinel formation is likely caused by Mn migration and O deficiency
- Raman spectroscopy suggest that the surface is transforming to a spinel like structure
  - Redox transitions between Ni<sup>2+</sup> and Ni<sup>4+</sup> undetectable after prolonged cycling
- Li<sup>+</sup> diffusivity in HCMR™ varies as a function of potential and correlates strongly with DC-R behavior
- FTIR spectroscopy indicates formation of a surface film composed of electrolyte decomposition products, which may create electronic and ionic barriers in the composite electrode
- SEM shows changes in the primary and secondary particles morphology
- Morphology and topology changes of the HCMR™ material and the electrode composite contribute to the long-term impedance rise with prolonged cycling